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**Identification of the Emission Features Near 3.5 μ m in
the Pre-main-sequence Star HD 97048**

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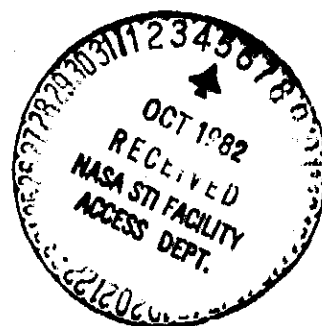
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Abstract

The spectrum of HD 97048 has been measured with a resolving power of 450 between 3.37 and 3.64 μ m. The prominent feature near 3.5 μ m, discovered by Blades and Whittet, is well resolved, with a peak at 3.53 μ m and a wing extending to shorter wavelength. The weaker feature near 3.4 μ m is found to peak at 3.43 μ m, in contrast to the 3.40 μ m feature seen in other astronomical objects. The observed spectrum strongly resembles laboratory spectra of mixtures of monomeric and dimeric formaldehyde embedded in low temperature solids. Of various possible excitation mechanisms, ultraviolet pumped infrared fluorescence of formaldehyde in interstellar grains provides the best explanation for

The spectra of HD 97048, ratioed to those of γ Cha, are shown in Figure 1. Other than an apparent overall decrease in flux in 1982, which is within our calibration uncertainties, the two spectra are virtually identical. The peaks of the two emission features occur at $3.53 \mu\text{m}$ and $3.43 \mu\text{m}$. The brighter feature at $3.53 \mu\text{m}$ has a full width at half maximum of about $0.035 \mu\text{m}$ and an asymmetric profile with a tail extending to shorter wavelengths. The drop-off from the peak to longer wavelengths is steep but resolved. The shorter wavelength feature is centered at $3.42 \mu\text{m}$, and has distinct peaks at $3.41 \mu\text{m}$ and $3.43 \mu\text{m}$. The $3.4 \mu\text{m}$ feature was identified by Blades and Whittet with the $3.4 \mu\text{m}$ feature seen in NGC 7027 and other sources. Aitken and Roche called attention to the unusual strength of the $3.4 \mu\text{m}$ feature in HD 97048 however; it is considerably brighter than the $3.3 \mu\text{m}$ feature, a situation reversed from that observed elsewhere, for example in NGC 7027. In addition, both grating spectra (Grasdalen and Joyce 1976b) and FTS spectra (Tokunaga and Young 1980) obtained at resolutions comparable to ours (10 cm^{-1} and 4 cm^{-1} , respectively, compared to our 6.3 cm^{-1}) show clearly that the feature in NGC 7027 is centered at $3.40 \mu\text{m}$, and has no peak at $3.43 \mu\text{m}$. It appears that the $3.40 \mu\text{m}$ feature, seen in conjunction with a $3.28 \mu\text{m}$ feature in many objects, contributes only a small part of the flux near $3.4 \mu\text{m}$ in HD 97048. A weak shoulder does appear at $3.40 \mu\text{m}$ in Figure 1; this may be the usual $3.40 \mu\text{m}$ feature.

Comparison of the spectra in Figure 1 with that published by Aitken and Roche (1981) reveals two interesting anomalies (see Table 1). First, the equivalent width of both features are higher in the Aitken and Roche data than in ours. Second, the ratio of the strength of the $3.4 \mu\text{m}$ feature to that of the $3.5 \mu\text{m}$ feature is considerably larger in the Aitken and Roche data. It would appear that the intensities of these features varied between January 1980 and April 1981. However, the equivalent widths in Blades and Whittet's spectrum agree

the observed spectrum of HD 97048.

Introduction

Attention was drawn to HD 97048, a likely pre-main-sequence star in the Chamaeleon T association, by Blades and Whittet (1980) who measured its 3-4 μm spectrum at a resolving power of ~ 50 and discovered a bright and broad emission feature near 3.5 μm . Although many astronomical objects display mid-infrared emission features, probably due to vibrational bands of molecules bound in grains (see review by Aitken 1981), the 3.5 μm emission feature appears to be quite rare. Allen *et al.* (1982) have made a survey of 56 emission-line stars and stellar planetary nebulae and detected 3.5 μm emission only from HD 97048 and Elias 1.

HD 97048 has a spectral type of B9-A0 V_e and illuminates a reflection nebula in the Chamaeleon dark cloud at a distance of ~ 150 pc from the sun. Variable hydrogen line emission (Irvine and Houk 1977) and an infrared excess (Grasdalen *et al.* 1975) both indicate that it is losing mass. In addition to the unusual 3.5 μm feature, HD 97048 shows emission features near 3.3, 3.4, and 11.3 μm (Blades and Whittet 1980; Aitken and Roche 1981), which are among those seen in other astronomical objects. The 3.3 and 11.3 μm features have an intensity ratio like that seen elsewhere, but whereas other objects have a weak 3.4 μm feature associated with that at 3.3 μm , the intensity ratio of these features is reversed in HD 97048. This suggests an additional contribution near 3.4 μm , perhaps from the same species which is responsible for the 3.5 μm feature.

Blades and Whittet suggested that the 3.4 and 3.5 μm features in HD 97048 could be due to formaldehyde (H_2CO) or polyoxymethylene ($\text{n-H}_2\text{CO}$). Aitken and Roche showed that the ultraviolet fluorescence mechanism of Allamandola and Norman (1978) could explain the 3.4 and 3.5 μm emission if 20% of the ultraviolet photons emitted by the star shortward of 200 nm resulted in fluorescence

in these bands. They were able to rule out polyoxymethylene however, because of the lack of an expected strong feature near $9\ \mu\text{m}$, and on this basis condemned the 3.4 and $3.5\ \mu\text{m}$ bands "to join the ranks of the unidentified."

In this paper, we present new spectroscopic observations of HD 97048 which resolve the 3.4 and $3.5\ \mu\text{m}$ features. Comparison of these observations with laboratory spectra lends further support to their identification with H_2CO . We also show that the existence of these features in this particular object is better explained by the ultraviolet-pumped fluorescence model of Allamandola and Norman (1978) than by the bimodal grain size model of Dwek *et al.* (1980).

Observations and Results

In order to better determine the profiles of the infrared emission features in HD 97048, we observed the source at higher spectral resolution than has been reported to date. The observations were carried out on the 2.5m du Pont telescope at Las Campanas Observatory, using the $1 - 5\ \mu\text{m}$ grating spectrometer described by Persson, Geballe and Baas (1982). The instrument was set up to give a spectral resolving power of 450 at $3.5\ \mu\text{m}$; this corresponds to a resolution of $6.3\ \text{cm}^{-1}$ or $0.0078\ \mu\text{m}$. Standard infrared chopping and beamswitching techniques were used; the entrance aperture was $8''$ in diameter, and the throw was $60''$. HD 97048 was observed in 1981 April and again in 1982 May. It was observed on several nights in 1981; the best pair of spectra are presented here. Two pairs of scans were measured in 1982. In order to correct for atmospheric absorption and to divide out the system response, we have ratioed the observed spectrum of HD 97048 to that of the nearby star γ Cha (MO III) which was observed through a similar air mass. At our spectral resolution, the atmospheric features in the γ Cha spectrum are between 15 and 25% deep, so we expect uncertainties due to residual atmospheric features to be no greater than 5%.

The spectra of HD 97048, ratioed to those of γ Cha, are shown in Figure 1. Other than an apparent overall decrease in flux in 1982, which is within our calibration uncertainties, the two spectra are virtually identical. The peaks of the two emission features occur at $3.53 \mu\text{m}$ and $3.43 \mu\text{m}$. The brighter feature at $3.53 \mu\text{m}$ has a full width at half maximum of about $0.035 \mu\text{m}$ and an asymmetric profile with a tail extending to shorter wavelengths. The drop-off from the peak to longer wavelengths is steep but resolved. The shorter wavelength feature is centered at $3.42 \mu\text{m}$, and has distinct peaks at $3.41 \mu\text{m}$ and $3.43 \mu\text{m}$. The $3.4 \mu\text{m}$ feature was identified by Blades and Whittet with the $3.4 \mu\text{m}$ feature seen in NGC 7027 and other sources. Aitken and Roche called attention to the unusual strength of the $3.4 \mu\text{m}$ feature in HD 97048 however; it is considerably brighter than the $3.3 \mu\text{m}$ feature, a situation reversed from that observed elsewhere, for example in NGC 7027. In addition, both grating spectra (Grasdalen and Joyce 1976b) and FTS spectra (Tokunaga and Young 1980) obtained at resolutions comparable to ours (10 cm^{-1} and 4 cm^{-1} , respectively, compared to our 6.3 cm^{-1}) show clearly that the feature in NGC 7027 is centered at $3.40 \mu\text{m}$, and has no peak at $3.43 \mu\text{m}$. It appears that the $3.40 \mu\text{m}$ feature, seen in conjunction with a $3.28 \mu\text{m}$ feature in many objects, contributes only a small part of the flux near $3.4 \mu\text{m}$ in HD 97048. A weak shoulder does appear at $3.40 \mu\text{m}$ in Figure 1; this may be the usual $3.40 \mu\text{m}$ feature.

Comparison of the spectra in Figure 1 with that published by Aitken and Roche (1981) reveals two interesting anomalies (see Table 1). First, the equivalent width of both features are higher in the Aitken and Roche data than in ours. Second, the ratio of the strength of the $3.4 \mu\text{m}$ feature to that of the $3.5 \mu\text{m}$ feature is considerably larger in the Aitken and Roche data. It would appear that the intensities of these features varied between January 1980 and April 1981. However, the equivalent widths in Blades and Whittet's spectrum agree

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well with our results, and we observed no change in the equivalent widths between 1981 and 1982. We also made spatial scans of HD 97048 in 1982 to test whether extended emission could cause the equivalent widths to be aperture dependent. No evidence of extension was seen, limiting the source size to less than 2" FWHM. Although we cannot be sure of the explanation for the discrepancy in measured equivalent widths, we note that there are six strong atmospheric absorption features across the 3.4 μm feature and none near 3.5 μm . If a part of the 3.4 μm feature were due to a narrow emission line, it could vary in intensity with the hydrogen lines or could move in and out of an atmospheric absorption feature with the earth's motion or with atmospheric variations.

Identification of the Features

On the basis of the wavelength coincidence alone, Blades and Whittet (1980) suggested that the 3.4 and 3.5 μm features in HD 97048 could be due to formaldehyde bound to grains. The higher resolution spectra presented here allow a more detailed comparison with laboratory spectra. Because the 3 μm vibrational bands of H_2CO bound in a solid show similar infrared and Raman spectra, either type of spectrum can be used for comparison with the astronomical observations. Raman spectra of the ν_1 and ν_2 fundamental modes of H_2CO (symmetric and antisymmetric C-H stretch respectively) embedded in argon and nitrogen matrices at 22K have been obtained by Khoshkhoo and Nixon (1973). Two representative spectra are shown in Figure 2. The peaks labeled M and D are due to formaldehyde monomers and dimers, respectively, and vary in relative intensity with the formaldehyde concentration in the samples. The laboratory spectra are very similar to those of HD 97048, supporting the identification of the 3.5 and 3.4 μm features with H_2CO . If this identification is correct, the wing on the blue side of the 3.5 μm feature would be due to dimers and possibly

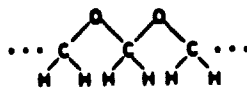
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other complexes of H_2CO . The structure in the $3.4 \mu\text{m}$ peak could also be due to monomeric and dimeric H_2CO .

Laboratory absorption studies by one of us (L. J. A.) have failed to find any other astrophysically plausible molecule with a pair of bands near 3.4 and $3.5 \mu\text{m}$. C-H stretching bands of non-aldehydic molecules generally occur at shorter wavelengths. It is also significant that infrared spectra of frozen mixtures of H_2O , CO , CH_4 , and NH_3 taken in the laboratory (by L. J. A. and F. B.) after photolysis by vacuum ultraviolet light have shown that a significant fraction (up to 10%) of the original mixture was converted into H_2CO and that the H_2CO was not readily photodissociated. These facts, coupled with the relative simplicity and known astrophysical presence of H_2CO further support our identification of the features in HD 97048.

Two differences between the laboratory and astronomical spectra are apparent and must be explained. First, both features are seen at higher frequency in the astronomical spectra; the stronger feature is shifted by 33 cm^{-1} . This shift is relatively small (1% of the band energy) and could be due to interaction of the H_2CO molecule with adjacent molecules in the grain. Observations of a shift of about one half the required amount as a result of hydrogen bonding to H_2O (see Table 2) indicate that a 33 cm^{-1} shift is not unreasonable. The ν_1 and ν_4 bands of associated H_2CO are in fact shifted by almost the required amount (Harvey and Ogilvie 1962; see Table 2) from those of gaseous H_2CO .

We note here a distinction between polymerized formaldehyde (polyoxymethylene or $n\text{-H}_2\text{CO}$) and associated formaldehyde. Polymerization of formaldehyde involves a change in the molecular structure, whereas association involves only relatively weak hydrogen bonding. The chemical structures of H_2CO and $n\text{-H}_2\text{CO}$ are:

 H_2CO  $n\text{-H}_2\text{CO}$

At the temperatures of interstellar grains individual H_2CO molecules can be stuck together without polymerizing. These complexed molecules, which are not free, but are perturbed by adjacent H_2CO molecules, are called "associated" by Harvey and Ogilvie.

The 8-13 μm spectrum of Aitken and Roche ruled out polyformaldehyde since the expected 9 μm band was not detected in their spectrum. However, isolated or associated H_2CO shows a much weaker absorption in this band (Harvey and Ogilvie 1962) which may have escaped detection. A weak feature is present in their spectrum at 8.6 μm , coincident with the ν_6 band of monomeric H_2CO (Khoshkhoo and Nixon). This evidence is not conclusive, however, as an 8.6 μm feature is seen in other objects which lack the 3.53 and 3.43 μm features. A better test of the proposed identification with H_2CO would be observation of the ν_2 C=O stretch band at 5.75 μm , although a non-detection would not necessarily imply the absence of H_2CO if more sensitive non-radiative processes play a role in deexciting the molecules.

A second difference between the laboratory and astronomical spectra is that the observed spacing between the two peaks in HD 97048 is 80 cm^{-1} , compared with the laboratory splitting of 65 cm^{-1} . Interactions with adjacent grain molecules may also explain this discrepancy, since the different vibrational modes could respond differently to interactions which constrain the formaldehyde molecule. The ν_4 band does shift more than the ν_1 band in being frozen in a matrix (Khoshkhoo and Nixon), although the splitting does not change in going from an argon to a nitrogen matrix or to the hydrogen bonded system of $\text{H}_2\text{O}:\text{H}_2\text{CO}$ in argon. Alternatively, the 3.4 μm feature in HD 97048 may be due to more than one species. It could for example be due to a 3.40 μm feature associated with the 3.28 μm band, a 3.45 μm feature due to H_2CO , and perhaps a third feature centered near 3.43 μm .

The identification of the 3.43 and 3.53 μm features as due to H_2CO would seem unlikely if a 3.5 μm feature which appeared for a short time in two novae (Grasdalen and Joyce 1978a, R. R. Joyce, private communication) were caused by the same species; it is unlikely that the grains flowing out from a nova could be sufficiently cold to allow H_2CO to condense. The spectral resolving power of the Nova Cyg data is high enough however ($\lambda/\Delta\lambda \sim 45$) that the 3.4 μm feature should have been seen easily; it should have looked much like that of Blades and Whittet's HD 97048 spectrum taken at a resolving power of 50. There is no evidence for any 3.4 μm feature in the nova spectra, however, indicating that the 3.5 μm feature seen there probably has a different origin from that seen in HD 97048.

Excitation Mechanisms

Two models appear most promising to explain the infrared emission bands generally; the ultraviolet-pumped infrared fluorescence model of Allamandola and Norman (1978) and the bimodal grain size model of Dwek *et al* (1980). In the Allamandola and Norman model, ultraviolet light is absorbed by molecules bound in the grains, leaving the molecules vibrationally excited. Some of the vibrationally excited molecules then radiatively decay before the vibrational energy can be distributed among other modes of the grains. Dwek *et al* argue that there are not enough ultraviolet photons to account for all of the infrared features, particularly those at the longer wavelengths, $\sim 10 \mu\text{m}$, which are observed from most astronomical sources showing these emission features. They instead suggest that two grain populations exist. Large, cool grains would account for the infrared absorption bands, whereas small hot grains would account for the emission features. The small grains could absorb ultraviolet radiation efficiently, but would be relatively inefficient at emitting infrared radiation except at resonant frequencies of bound molecules. This hypothesis for

the excitation mechanism for the unidentified emission features has recently been criticized by Olofson(1982) who argues that the observed emission at $3.28\ \mu\text{m}$ in two well studied sources implies a much higher flux in the $10\ \mu\text{m}$ region than has been observed, unless the resonant emitters possess abnormally strong intrinsic band strengths.

Dwek *et al* argue that because the $3.3\ \mu\text{m}$ feature is so often associated with the other features it must be excited in the same way. These arguments probably do not apply to the particular case of HD 97048, however. The $3.5\ \mu\text{m}$ feature is nearly unique to this object so it need not be excited in the same way as the other features. In addition, other aspects of the spectrum of HD 97048 make it difficult to explain the $3.5\ \mu\text{m}$ feature by thermal emission from grains. The infrared excess from HD 97048 is apparently dominated by grains with temperatures of about ~ 800 to $1200\ \text{K}$ (Grasdalen *et al* 1975; Glass 1979). A considerably cooler grain component is required for the $3.5\ \mu\text{m}$ feature, however, as H_2CO evaporates quickly at $\sim 200\ \text{K}$. Since the cool grains which could emit the $3.5\ \mu\text{m}$ feature contribute very little of the $3.5\ \mu\text{m}$ continuum radiation, the feature would have to have an unreasonably large equivalent width in the cool grains.

The ultraviolet-pumped fluorescence model can in principle have the required high quantum yields for conversion of ultraviolet photons into infrared photons, provided that the excited vibrational states do not quickly decay into the phonon modes of the grains. The efficiency of this mechanism is therefore critically dependent on the lifetimes of the excited states. These lifetimes depend on the strength of the coupling of each mode to the lattice and decrease as the temperature of the grains increases. In this model, mode dependent non-radiative relaxation processes can account for the weakness of the $9\ \mu\text{m}$ band while the $3.5\ \mu\text{m}$ band remains strong.

The ultraviolet radiation from HD 97048 can be converted efficiently into infrared emission from frozen H_2CO since the radiation from this A0 star peaks near 300 nm while solid H_2CO absorbs over a broad band shortward of 380 nm (McQuigg and Calvert 1969). The total flux emitted shortward of 380 nm is $\sim 1 \times 10^{-14} \text{ W cm}^{-2}$, a factor of five larger than calculated by Aitken and Roche who included only wavelengths shortward of 200 nm. Consequently, the energy conversion factor per H_2CO molecule can be as low as 3×10^{-3} to account for the observed 3.4 and 3.5 μm fluxes.

The low grain temperatures which are required for H_2CO to remain frozen in grain mantles points to the reflection nebula around HD 97048 as the source of the 3.4 and 3.5 μm emission. Our spatial scans of the source at the peak of the 3.5 μm emission feature argue against this interpretation, however. The emission was observed to be extended over no more than $2''$, which corresponds to 300 A.U., or 1.5×10^{-3} pc. To obtain an adequate number of grains in a column of length 300 A.U. (assuming the emitting column to be no longer than it is wide) would require a cloud density of $\geq 10^8 \text{ cm}^{-3}$, for a normal gas to dust ratio, and a band oscillator strength of $f \leq 1$. As HD 97048 is clearly not embedded in a dense molecular cloud, it appears that the emitting grains must be of circumstellar origin. These grains could either have formed in the gas flowing out from the star or be contained in remnant protostellar material. In either case the grains would probably have to be contained within dense condensations in order that they be sufficiently cool to allow H_2CO to be bound within their mantles. With no shielding from the stellar radiation, grains at 300 A.U. from an A0 V star would have temperatures between ~ 100 and 300K, depending on their absorption and emission properties. Although we know of no unambiguous way to choose among the various origins of the grains, the possibility of dense condensations within a protostellar nebula seems particularly interesting as a likely

stage in the formation of a planetary system. Such a short-lived phase would also provide a natural explanation for the rarity of the $3.5\ \mu\text{m}$ feature.

Conclusion

The 3.4 and $3.5\ \mu\text{m}$ emission features in HD 97048 have been remeasured with a spectral resolving power of 450. The feature profiles, which are now resolved, support the assignment to H_2CO . This assignment and the observed fluxes are difficult to reconcile with the thermally induced resonance radiation model of Dwek *et al.* On the other hand, it does appear possible to explain the observations by ultraviolet-stimulated infrared emission from H_2CO frozen on grains. This model requires inefficient conversion of vibrational excitation into thermal modes of the grains. Laboratory experiments are now in progress to measure the relative rates of radiative and non-radiative deexcitation of H_2CO and other molecules frozen in solids. The small observed angular extent and required low grain temperatures suggest that the emitting grains are in condensations in circumstellar, and possibly protostellar, material.

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Table 1

<u>Observed Equivalent Widths</u>				
<u>Date</u>	$w_{\lambda}(3.4)$	$w_{\lambda}(3.5)$	$w_{\lambda}(3.4)/w_{\lambda}(3.5)$	<u>reference</u>
1979 Mar	0.06 μm	0.10 μm	0.6	Blades and Whittet
1980 Jan	0.12	0.145	0.8	Aitken and Roche
1981 Apr	0.06	0.115	0.5	this paper

Table 2

<u>H₂CO Band Frequencies in Solids</u>						
<u>Monomer</u> ^a			<u>H₂CO: H₂O</u> ^b	<u>Dimer</u> ^a	<u>Associated</u> ^c	<u>HD 97048</u> ^d
gas	Ar	N ₂	Ar	Ar	Ar	
2782	2797	2800	2817	2810	2829	2833
2843	2863	2865	2884	2873	2885	2915

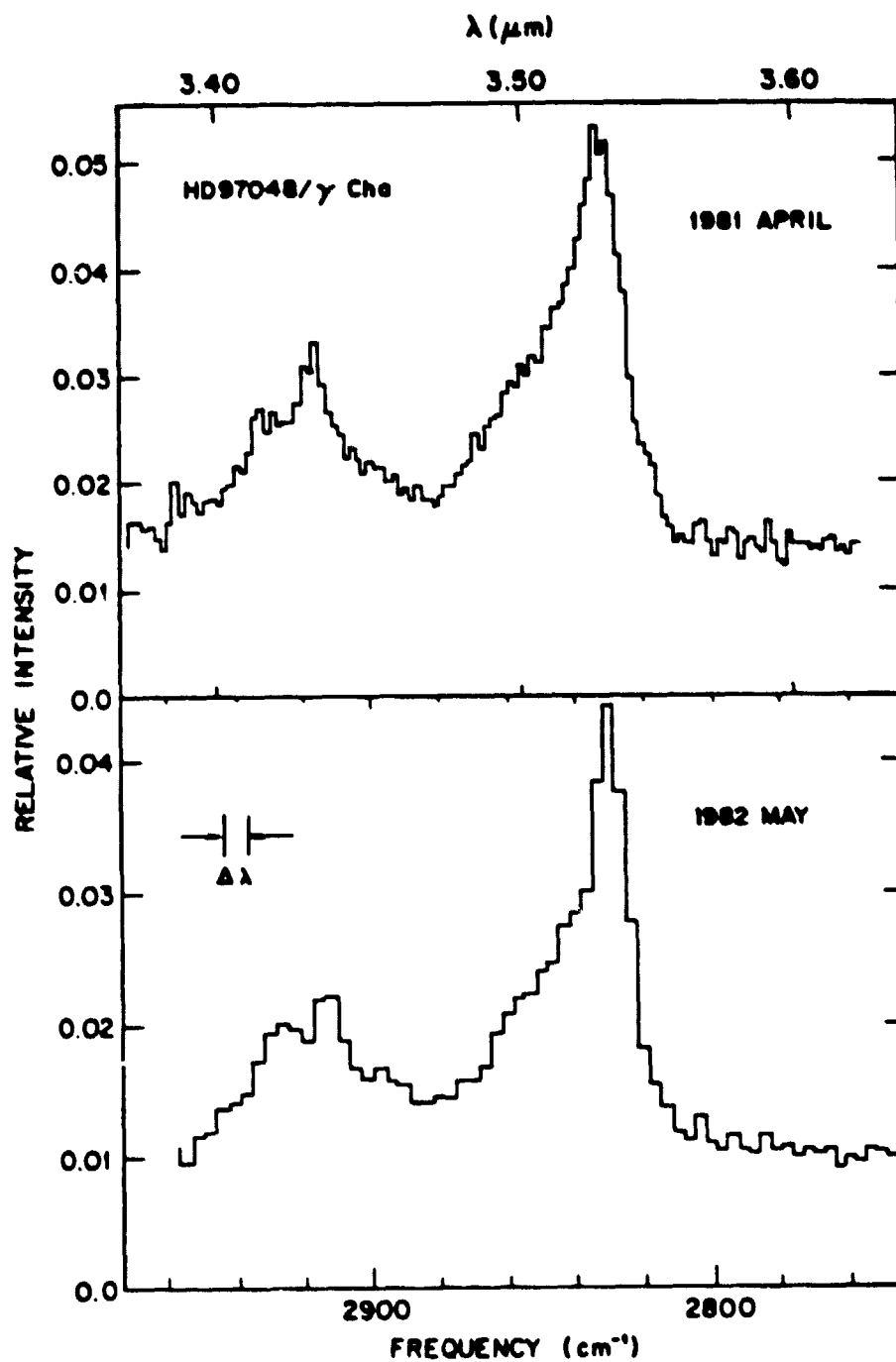
references: a) Khoshkhoo and Nixon 1973; b) Nelander 1980;
c) Harvey and Ogilvie 1962; d) this paper

Figure Captions

Figure 1. The 3.37 to 3.64 μm spectrum of HD 97048 ratioed to that of γ Cha, as observed with a spectral resolution $\Delta\lambda$ of 0.0078 μm ($\lambda/\Delta\lambda = 450$). The 1981 spectrum was sampled at 0.002 μm intervals, the 1982 spectrum at 0.004 μm intervals.

Figure 2. Raman spectra of H_2CO in solid argon (top figure) and nitrogen (lower figure) recorded at 22K, reprinted from Khoshkhoo and Nixon (1973). Features due to monomeric and dimeric H_2CO are indicated by M and D, respectively.

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